A review of preparation of binderless fiberboards and its self-bonding mechanism

Daihui Zhang[1,2] · **Anjiang Zhang**[1] · **Lixin Xue**[1]

Received: 18 December 2014

Abstract The demand for fiberboards has been growing in recent years. However, emission of formaldehyde, which was the main component of adhesives in fiberboards, has caused environmental and health concerns. Industries are therefore pursuing green chemistry technologies to eliminate these concerns. Binderless fiberboards appeared to be such candidates since the manufacturing process involved no resin addition. Several potential mechanisms of the formation of binderless fiberboards have been proposed. Chemical changes of components in lignocellulosic materials were expected to occur, and self-bonding achieved during hot pressing provided main bonding strength. This review summarized various aspects of binderless fiberboard production, particularly feasibility of different raw materials, chemical and enzymatic pretreatments of raw materials, manufacturing process, as well as the potential mechanism of self-bonding. Furthermore, further work that may benefit the elucidation of self-bonding mechanism was discussed.

✉ Anjiang Zhang
zhanganjiang@nimte.ac.cn

✉ Lixin Xue
xuelx@nimte.ac.cn

[1] Polymer and Composite Division, Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, No. 1219, West Zhongguan Road, Zhenhai District, Ningbo 315201, Zhejiang Province, People's Republic of China

[2] Department of Bioresource Engineering, Macdonald Campus of McGill University, 21,111 Lakeshore Road, Sainte-Anne-De-Bellevue, QC H9X 3V9, Canada

Introduction

The presence of adhesives is traditionally essential for fiberboard manufacture to keep proper physical and mechanical properties. Formaldehyde, one of the most common components in adhesives, has been widely employed in the industry due to its low cost and desirable performance (Saheb and Jog 1999; Sreekala et al. 2000; Zadorecki and Michell 1989). However, the emission of formaldehyde from fiberboards gave rise to environmental and health concerns (Salthammer et al. 2010). Recently, formaldehyde has been reclassified into carcinogenic category 1B according to labeling and packaging of substances and mixtures (CLP) regulation in June 2014 in Europe (Regulation 605/2014). In order to eliminate these concerns, formaldehyde-free adhesives made from natural resources, including lignin (Mansouri et al. 2007; Yau et al. 2006), soy protein (Kumar et al. 2002), wheat protein (Schopper and Kharazipour 2006; Nikvash et al. 2012, 2013) and starch (Imam et al. 2001), have been extensively researched. However, high cost and relatively poor performance limited their application in the industry (Zhang et al. 2014b). Therefore, the production of fiberboards without adhesives addition is a promising strategy from economic and environmental perspectives. Earlier researches have demonstrated the feasibility of bark as raw materials to produce binderless fiberboards (Chow 1975; Wellons and Krahmer 1973). However, the requirement for high pressing temperature as one of the main obstacles limited their application and development (Chow 1972; Gupta et al. 2011). Recently, binderless fiberboards made from refined bark of black spruce have been obtained. However, fabrication of wood fibers and bark in a sandwich structure was needed to obtain acceptable results (Gao et al. 2011). Systematic researches on binderless fiberboards could be traced back to 1980s. Mobarak et al. (1982) prepared binderless lignocellulose composite from bagasse, and the potential mechanism of self-bonding was discussed. Later on, Shen (1986) proposed and patented a process for the production of binderless fiberboards, which made its industrialization possible. Different raw materials, such as coconuts (Van Dam et al. 2004), oil palm (Baskaran et al. 2012) and bamboo (Shao et al. 2009), have been studied to determine their feasibility in the production of binderless fiberboards. Chemical and enzymatic pretreatments of raw materials provided new avenues toward the improvement of properties of binderless fiberboards, owing to their ability to form free radicals on the surface of fibers (Felby et al. 1997a, b; Kharazipour et al. 1997; Riquelme-Valdes et al. 2008; Widsten 2002; Hüttermann et al. 2001; Müller et al. 2009; Mai et al. 2004; Kües et al. 2007). Additionally, manufacturing processes concerning steam explosion before hot pressing and steam injection explosion have been developed and suggested to generate more reactive sites contributing to self-bonding, which in turn improved the performance of binderless fiberboards to meet established industrial standards (Quintana et al. 2009; Widyorini et al. 2005c).

However, discussions or results of the production of binderless fiberboards are most limited on laboratory level. The reason behind this is that the mechanisms of self-bonding formation during the production of binderless fiberboards have remained elusive. Therefore, elucidation of self-bonding mechanism is beneficial

for further improvement of performance of binderless fiberboards and thus their industrialization. Several potential explanations have been proposed: lignin–furfural linkages (Suzuki et al. 1998), condensation reaction in lignin (Okuda et al. 2006b) and furfural self-polymerization (Yan et al. 1996). Furthermore, physical phenomenon involving thermal softening of lignin has also been suggested to be partially responsible for fiberboards formation (Bouajila et al. 2005). Actually, the mechanism behind this process varies depending on raw materials and manufacturing process. Moreover, reactions and phenomenon mentioned above are expected to work collaboratively for the production of binderless fiberboards. Large varieties of studies have been conducted to elucidate the self-bonding mechanism by means of several tools, such as Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) and gas chromatography–mass spectrometry (GC-MS) to determine the composition changes of binderless fiberboards (Okuda et al. 2006b; Xu et al. 2006). While these analyses revealed chemical changes in binderless fiberboards before and after pressing, no detailed information on specific or functional group changes during the pressing could be found. Pressing is a dynamic process. Its variables regarding temperature and pressure generally fluctuate as the time changes. Therefore, it is necessary to understand the correlation between changes of groups and fluctuation of variables. Importantly, these works would benefit the optimization of manufacturing process. X-ray photoelectron spectroscopy (XPS) seems to serve as such a purpose since it has been used to study the surface chemical compositions of cellulosic fibers before and after esterification (Matuana et al. 2001). Detailed information will be discussed later.

Summarily, different raw materials were reviewed which have been employed in the production of binderless fiberboards. Chemical and enzymatic pretreatments of raw materials have also been discussed. After a discussion of manufacturing process, self-bonding mechanism of binderless fiberboards as one of the most important aspects was covered. Finally, future work that may deserve attention has been proposed.

Resources of raw materials

Not all lignocellulosic materials are suitable for the production of binderless fiberboards which is economically attractive for commercialization. Attentions have been put on woody fibers as a raw material since binderless fiberboards were successfully obtained from two different types of fiber furnishes (Suchsland et al. 1985). Furthermore, other resources, such as bagasse, flax and corn, have been patented to make fiberboards without resin addition (Shen 1986). Therefore, the resources were classified into woody and non-woody raw materials. They are described in the following sections.

Woody raw materials

In most cases, high amounts of cellulose and lignin but low hemicelluloses content were found in woody materials. Consequently, wood-based composites exhibited a

better resistance to water than other non-woody materials due to the fact that hemicelluloses are hydrophilic and able to adsorb water (Ye et al. 2007). On the other hand, synthetic resins are usually used for the production of wood-based fiberboards because of weak bonding strength which maybe result from the low hemicelluloses content as well. Specifically, residues of spruce and pine have been examined for their potential in producing binderless fiberboards (Anglès et al. 2001; Angles et al. 1999). Steam explosion pretreatment was applied in order to determine their effect on board properties. It turned out that steam explosion was beneficial for the improvement of physical properties of fiberboards. Other woody materials, such as *Pinus radiata* (Riquelme-Valdes et al. 2008), spruce fibers (Widsten et al. 2003), beech and rubber fibers (Felby et al. 1997a, 2004; Nasir et al. 2013), have also been evaluated in the production of binderless fiberboards. However, all woody fibers suffered from enzymatic or chemical pretreatment to generate more stable radicals which were able to initiate self-bonding between fibers. While poplar fibers showed their potential to prepare binderless fiberboards, the addition of enzymatic hydrolysis lignin was conducted to improve the properties of fiberboards (Zhou et al. 2013). Recently, the authors' group has patented a method to produce binderless fiberboards with high density and thickness and observed that procedure to control the size of cross section and length of wood fibers was essential for their production (Zhang et al. 2013). In general, binderless fiberboards made from woody raw materials seem to necessarily combine other treatments, such as steam explosion pretreatments and surface activation of fibers. The addition of wax or lignin maybe acts as an alternative option to keep acceptable dimensional stability without compromising bonding strength.

Non-woody raw materials

Due to increasing wood price and shortage of wood supply, alternative sources of raw materials for the production of fiberboards are needed. Lignocellulosic wastes including bagasse (Shen 1986; Widyorini et al. 2005a), coconut husk (Van Dam et al. 2004) and wheat straws (Halvarsson et al. 2009) have been explored due to their low price and richness. Velasquez et al. (2003) produced binderless fiberboard from *Miscanthus sinensis*, and the obtained fiberboards exhibited desirable performance under optimized conditions after steam explosion pretreatment. The suitability of banana bunch has also been evaluated. Raw materials were steam exploded and then used to make binderless fiberboard (Quintana et al. 2009). However, low IB and high thickness swelling (TS) values were observed, and it could probably be related to lignin structure of banana bunch and high residual xylose content, respectively. Furthermore, it was suggested that the grinding process before the pressing stage was able to significantly improve IB without compromising other physical–mechanical properties of fiberboards from steam-exploded *Miscanthus sinensis* (Velasquez et al. 2002). Recently, the potential of seed cake as raw material was investigated for the production of fiberboards, and the mechanical properties are comparable with typical commercial fiberboards under optimized conditions (Hidayat et al. 2014). Obviously, chemical compositions of raw materials determined their suitability in the production of binderless fiberboards. Varieties of

Table 1 Summary of non-woody raw materials in the production of binderless fiberboards

Resources	Manufacturing process	Other treatments	References
Plantain	Hot pressing	Laccase	Álvarez et al. (2011)
Coconuts	Hot pressing	N/A	Van Dam et al. (2004)
Wheat straw	Hot pressing	Fenton's reagent	Halvarsson et al. (2009)
Miscanthus sinensis	Hot pressing	Steam explosion/lignin addition	Velasquez et al. (2003)
Banana bunch	Hot pressing	Steam explosion	Quintana et al. (2009)
Seed cake	Hot pressing	N/A	Hidayat et al. (2014)
Cotton stalks	Hot pressing	N/A	Fahmy and Mobarak (2013)
Bamboo	Hot pressing	Steam explosion	Shao et al. (2009)
Kenaf core	Hot pressing	N/A	Okuda et al. (2006a)
	Steam injection	N/A	Xu et al. (2006)
Vitis vinifera	Hot pressing	Steam explosion/alkaline lignin	Mancera et al. (2011)
Cynara cardunculus	Hot pressing	Steam explosion	Mancera et al. (2008)

non-woody raw materials used in the production of binderless fiberboards are summarized in Table 1. In summary, poor dimensional stability of binderless fiberboards made from non-woody materials was one of the biggest drawbacks resulting from high hemicelluloses content. The extension of steam pretreatment seemed to be an option to overcome this drawback, but correspondingly, the energy consumption has to be considered.

Pretreatment of raw materials

It was well known that adhesives were able to enhance fiber interaction providing desirable mechanical and physical properties. Therefore, the production of fiberboards without synthetic resin was challenging. Chemical pretreatments, such as alkaline, acid and oxidation agents, have been utilized in the activation of fiber surface (Anglès et al. 2001; Geng et al. 2006; Schmidt et al. 2002; Young et al. 1985). Binderless fiberboards made from alkaline-treated black spruce bark possessed a higher IB, modulus of rupture (MOR) and modulus of elasticity (MOE) than those of untreated samples (Geng et al. 2006). Compositions analysis revealed the occurrence of de-acetylation of wood fibers, as well as degradation of large amounts of lignin and hemicelluloses (Schmidt et al. 2002). These changes might explain the positive effect of alkaline treatment on the mechanical properties of binderless fiberboards. On the other hand, acid treatment was usually considered as a prehydrolysis before steam explosion due to its significant effect on the structure of raw materials (Anglès et al. 2001). It was suggested that nitric acid activation of wood surfaces involved oxidation, nitration and hydrolysis of wood polymers (Rammon et al. 1982; Subramanian et al. 1982; Young et al. 1982). Therefore, the concentration and treatment time of alkaline and acid need to be

carefully controlled in order to avoid excessive degradation of main components in raw materials. In this section, Fenton's reagent and laccase treatments were emphasized due to their possibilities in realization of the production of binderless fiberboards with satisfactory performance. Finally, addition of other components was also included considering their potential effect on the performance of binderless fiberboards.

Chemical pretreatment of raw materials

Fenton's reagent

Fenton's reagent composed of ferrous chloride and hydrogen peroxide could activate the fiber surface. This oxidation pretreatment facilitated the adhesive bonding between fibers. The main reaction process was shown in the following equation:

$$RH + OH\cdot \rightarrow H_2O + R\cdot$$

where hydroxyl radicals (OH·) was continuously generated by decomposition of hydrogen peroxide with the assistance of ferrous ions. Then, these hydroxyl radicals were capable of reacting and attacking fibers and lignin to form reactive components (R·). The activated components were able to covalently bond with low-molecular degraded components contributing to self-bonding in binderless fiberboards (Kharazipour et al. 1998). On the other hand, intra-fiber crossing links were also created due to the diffusion of degraded low-molecular reagents into lumen within cell walls. These intra-fiber links are believed to increase the dimensional stability of fiberboards (Halvarsson et al. 2009; Widsten 2002).

Halvarsson et al. (2009) investigated the physical and mechanical properties of binderless fiberboards made from Fenton's reagent-treated wheat straw. The strength of fiberboards was further enhanced, and TS of fiberboards decreased when hydrogen peroxide percentage was increased from 2.5 to 4.0 %. Specifically, TS and water adsorption (WA) of the fiberboards with best performance prepared with 4.0 % hydrogen peroxide and 2 % addition of $CaCl_2$ were 75 and 90 %, respectively (Halvarsson et al. 2009). Furthermore, oil palm was subjected to Fenton's reagent oxidation (4 %, H_2O_2), and the treated fibers were then used to prepare binderless fiberboards at a pressing temperature of 190 °C. TS and WA of obtained fiberboards were 35 and 48 %, respectively, which were lower than those of fiberboards made from treated wheat straw (Mejía et al. 2014). Comparison of results indicated that the chemical components of different raw materials were a key factor for their suitability in the production of binderless fiberboards. While this method seemed to be an interesting direction of research, there were several weaknesses in terms of long-term harmful effect on the properties of fiberboards due to high peroxide charges, instability of board quality and insufficient mechanical strength unless high board densities (Widsten 2002).

Enzymatic pretreatment of raw materials

The interest in enzymatic treatments of cellulosic fibers is recently growing (Kharazipour and Euring 2010, 2013; Euring et al. 2011a, b; Kudanga et al. 2011). Compared with chemical treatments, enzymatic treatment often involves mild reaction condition, less by-products and being environmentally friendly (Euring et al. 2013). Laccase, which is widely distributed in plants and fungi, has been intensively studied in the pulp and paper industry. It can catalyze the oxidation of various phenolic substrates (Nyanhongo et al. 2010; Kudanga et al. 2008; Pereira et al. 2005). During the fiber treatments, laccase hardly penetrated into fibers and mainly oxidized the lignin on the surface (Álvarez et al. 2011). As a result, free radicals were generated on the fiber surface. These free radicals can act as potential reactive sites for further cross-linking reactions in the production of fiberboards. The increase in molecular weight of lignin obtained from the surface of laccase-treated fiberboards strongly indicated the occurrence of polymerization of lignin (Felby et al. 2002). In the following equation, this process is described.

$$4\text{Phe-OH} + O_2 \xrightarrow{\text{Laccase}} 4\text{Phe-O}\cdot + 2H_2O$$

Laccase pretreatment of beech fibers promoted their adhesion, and the obtained fiberboards possessed a significantly higher strength than that of untreated fibers. Depositions of lignin and formation of covalent bonds between fibers were believed to be highly responsible for improved bonding (Felby et al. 2004). Scanning electron microscope (SEM) results of treated and untreated rubber fibers showed that enzyme-treated rubber fibers looked smooth due to lignin removal and breakdown of surface molecules in comparison with rough surface of untreated fibers (Fig. 1). Nasir et al. (2013) fabricated binderless fiberboards from rubber fibers treated at 9 U/g enzymes for 60 min and pressed at 200 °C. It showed acceptable performance in terms of MOE, MOR and IB, but not WA and TS. Furthermore, it was suggested that the amounts of enzyme should be controlled in order to avoid excessive removal of lignin, resulting in a dramatic decrease in IB (Nasir et al. 2013). Recently,

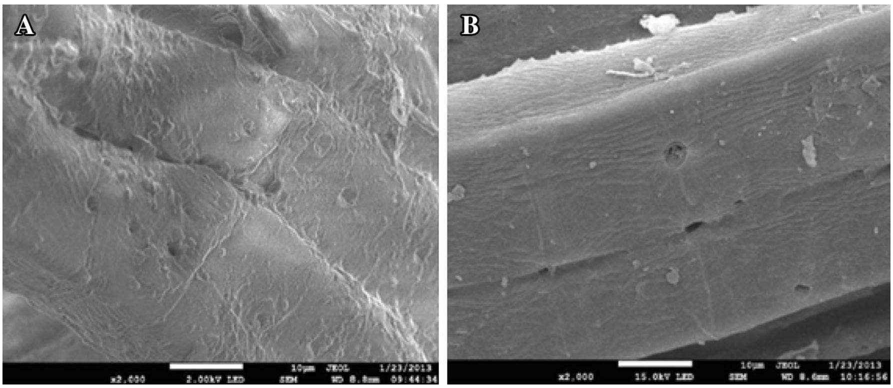

Fig. 1 SEM results of untreated fibers (**a**) and treated fibers (**b**) (Nasir et al. 2013)

manufacture of binderless fiberboards from enzyme pretreated lignocellulosic fibers has been reviewed, covering the effect of preheating temperature and wood type on fiberboard properties, as well as the evaluation of production methods (Widsten and Kandelbauer 2008; Mai et al. 2004). While enzymatic pretreatment has the potential to improve bonding strength, the attempts to industrially produce binderless fiberboards were difficult due to the presence of technical and economic problems, such as easy inactivation of enzyme under harsh conditions, the cost of enzyme and high investment of facilities.

Addition of other compositions

Lignin is a component which naturally provides adhesion in wood structure. Lignin-based wood adhesives have been prepared and applied in board industry (Mansouri et al. 2007). In the production of binderless fiberboards, lignin plasticization and cross-linking reaction between lignin and furfural have been considered to be partially responsible for board adhesion (Bouajila et al. 2005). Therefore, the addition of lignin was regarded as an effective method to enhance board properties. Anglès et al. (2001) have presented the effect of addition of several kinds of lignin on board performance, and it turned out that dimensional stability and mechanical characteristics were significantly improved. Kraft lignin acted as the best candidate. With addition of kraft lignin (20 % dry solid basis) to pretreated materials, TS and WA decreased from 12.9 ± 1.2 to 2.0 ± 0.6 % and 38 ± 7.0 to 7.0 ± 0.3 %, respectively. Lignin could work as a plastic and resist water penetration, which then improves the dimensional stability of fiberboards. Moreover, the improvement of mechanical properties of fiberboards could be attributed to the fact that lignin as an adhesive provided more reactive sites, thus increasing the links between cellulose fibers (Anglès et al. 2001). Similar conclusion was observed that the addition of kraft lignin prior to pretreatment improved the properties of binderless fiberboards made from steam-exploded *Miscanthus sinensis*. However, when the lignin was added after pretreatment, bubbles were observed at a high pressing temperature, which negatively influenced the properties of fiberboards. Oppositely, no bubbles were observed when adding lignin before pretreatment probably due to the better mixing and removal of low molecular weight compounds (Velasquez et al. 2003). Recently, binderless fiberboards made from poplar fibers with addition of enzymatic hydrolysis lignin (EHL) exhibited significantly improved physical and mechanical properties. These lignins were produced by enzymatic hydrolysis of pretreated substrates to remove carbohydrates. However, oxygen-related functional groups and radicals were further generated in EHL due to their subjection to oxygen plasma treatment (Zhou et al. 2013).

In the production of binderless particleboards, sugars have also been considered as effective additive to improve the properties. After adding 20 % glucose to oil palm biomass, MOR and IB were improved roughly from 5.0 to 13.5 MPa and 0.6 to 1.7 MPa, respectively. TS and WA values also significantly decreased with the addition of glucose (Lamaming et al. 2013). Briefly, the addition of other components was a promising method to improve the properties of boards in association with other pretreatments.

Manufacturing process

Two distinct methods have been widely utilized in the production of fiberboards, namely “wet-forming” process and “dry-forming” process. Wet-forming process involves the distribution of cellulosic materials into water. Hydrogen bonds formation and thermosetting adhesive behavior of lignin are expected during heating and drying processes. Accordingly, less or none binders are needed. However, low density and limited strength of fiberboards, along with waste water pollution are the main disadvantages of this process. In dry-forming process, moisture content of cellulosic materials is reduced via drying before combination with resins. After distribution of mixture into mat, it undergoes prepress and hot pressing to finally produce fiberboards. While a wet process to produce binderless fiberboards from a combination of fibers and particles has been recently patented (Lee and Hunt 2013), industrial manufacture of binderless fiberboards is mainly based on dry-forming process without resins addition. Furthermore, other processes such as steam explosion before hot pressing and steam injection pressing have been developed to increase the performance of binderless fiberboards. The main difference between steam explosion before hot pressing and conventional dry-forming process was the employment of steam explosion to efficiently expose components for further reaction in hot pressing. In the authors’ groups, microwave pretreatment has recently been further applied to the dry-forming process. It was observed that temperature of raw materials before pressing was rapidly increased with the assistance of microwave heating, and binderless fiberboards with a high density and thickness, as well as acceptable properties, were obtained (Zhang et al. 2014a). Detailed discussions about the current manufacturing process methods are presented in this section.

Steam explosion before hot pressing

Preparation of binderless fiberboards traditionally undergoes hot pressing process. However, the fiberboards produced only under hot pressing generally showed poor performance in terms of water adsorption and thickness swelling. Although the addition of wax into fibers has been suggested to overcome this drawback (Felby et al. 2002), steam explosion has been known as a more effective method to improve the dimensional stability of binderless fiberboards (Luo et al. 2014). It was able to liberate lignin from inside of cell wall to the fiber surface. SEM analysis of broken fiberboards obtained from mixture of softwood residues indicated that liberated lignin covered hemicelluloses and cellulose, which limited these two hydrophilic polymers to adsorb waters. Consequently, the dimensional stability of binderless fiberboards was improved. It also suggested that steam pretreatment had the ability to cause de-fibration and generate numerous shrinkage folds on the surface. These changes facilitated the adhesion behavior owing to the increase in contact surface. In addition, lignin droplets were observed on the surface of fiber. It was believed that the softening point of these droplets was lower than original lignin, easily resulting in occurrence of plastic flow of lignin (Angles et al. 1999). Angles et al.

(1999) related pretreatment severity of steam to treatment time and temperature. Its effect on the properties of binderless fiberboards produced from steam-exploded residual softwood revealed that high severities within a certain range were able to correspondingly improve the physical and mechanical properties of fiberboards. The addition of acid during steam pretreatment promoted further hydrolysis of hemicelluloses and cellulose. As a result, WA and TS of fiberboards decreased. Furthermore, short fibers packed more compactly preventing water from penetrating into matrix, which also decreased WA and TS (Anglès et al. 2001).

Steam explosion could also be applied to non-woody materials. *Miscanthus sinensis* was first subjected to steam explosion and then used to produce binderless fiberboards (Velasquez et al. 2003). Some basic parameters, especially TS and WA, met the requirement of relevant standard specifications. The increase in dimensional stability of the fiberboards is highly related to the decrease in hemicelluloses content (Velasquez et al. 2003). Saari et al. (2014) investigated the properties of steam-exploded binderless particleboards made from oil palm trunks. They observed that steam pretreatment could enhance the overall physical and mechanical characteristics of samples. As the increase in stream temperature and time, MOR and IB of fiberboards increased, and the values of TS and WA decreased. However, when increasing steam exposure time to 50 min, particle structure was destroyed, leading to reduction in strength properties. Therefore, longer steam exposure time was not recommended (Saari et al. 2014).

Shao et al. (2009) have systematically characterized lignin obtained from steam-exploded bamboo. Thermal gravimetric analysis (TG) and DSC analysis revealed that steam explosion showed the ability to decompose lignin since softening temperature of lignin was lower than that of original lignin. Cleavage of β-O-4 linkages in lignin confirmed by ozonation and NMR analysis was observed (Shao et al. 2009). Considering that the generation of β-O-4 linkages has been reported during the hot pressing (Saari et al. 2014), it was suggested that steam treatment exposed more reactive sites of phenolic hydroxyl ends and that reaction between these sites are expected to contribute to self-bonding in the formation of binderless fiberboards. Although evidences of positive effect of steam pretreatment on the production of fiberboards have been found, drawbacks of this process involving high water and energy consumption should not be ignored.

Hot pressing

The chemical components in biomass were able to achieve self-bonding under hot pressing. Therefore, pressing parameters such as temperature, time and pressure definitely influenced the properties of fiberboards. The effect of pressing temperature on the properties of binderless boards made from different raw materials such as oil palm truck and frond (Hashim et al. 2010; Laemsak and Okuma 2000; Saadaoui et al. 2013), kenaf core (Okuda et al. 2006b) and *Miscanthus sinensis* (Velasquez et al. 2003) have been examined. It turned out that pressing temperature is one of the most important manufacturing parameters affecting the properties of boards. As the pressing temperature increases, MOR and IB were observed to increase and WA and TS of the fiberboards decreased. Similarly, Boon

et al. (2013) concluded that increase in temperature, time and pressure had the potential to improve the mechanical strength and stability of fiberboards against moisture. Pressing temperature seemed to be the most significant parameter, whereas pressure and pressing time did obviously not affect the properties of fiberboards. The temperature should be limited to below 200 °C in order to avoid severe burning. Given the energy consumption, a high pressing temperature is also not recommended. Therefore, further improvement of dimensional stability via the increase in temperature was not effective (Boon et al. 2013). In addition, the presence of water in raw materials is crucial for the heat transfer during hot pressing. Effect of water content in feed materials (5–20 wt %) on the properties of fiberboards suggested that the optimum condition was 8 wt% moisture content, and higher moisture contents gave a negative effect on modulus (Hidayat et al. 2014).

Steam injection pressing

Researches on steam injection pressing in large panel fabrication with southern hardwoods were carried out about 30 years ago (Geimer and Price 1987). Afterward, this technology was employed to produce binderless fiberboards from mixed softwood and hardwood. It turned out that there was a poor bonding strength, whereas the dimensional stability of fiberboards was improved (Okamoto et al. 1994). Recently, few researches on steam injection pressing in the production of binderless fiberboards can be found (Kwon and Geimer 1998; Troughton and Lum 2000; Xu et al. 2005). Conversely, successful development of particleboards from kenaf core using steam injection pressing has been reported (Xu et al. 2003). The particleboards showed higher IB value (0.43 MPa, 0.50 g/cm^3) and lower average TS (11 %, 0.50 g/cm^3) than those of particleboards made under hot pressing, where IB was 0.09 MPa and average TS was 169 %. They also observed that mechanical properties of particleboards increased linearly with increasing board density. Furthermore, increase in steam pressure improved the bonding strength. Extension of steam treatment time from 7 to 15 min at a pressing pressure of 1.0 MPa decreased TS from 16 to 9.4 %, but had less effect on MOR.

Widyorini et al. (2005c) further compared the effect of steam injection and hot pressing on the chemical changes of kenaf core in the production of particleboards. It was suggested that mild steam injection (0.6–1.0 MPa, 7–20 min) gave rise to a significant degradation of lignin, cellulose and hemicelluloses compared with low-degree degradation under hot pressing. With a steam pressing pressure of 1.0 MPa, the mean TS was 7.47 % in contrast to 169 % of TS under hot pressing at 190 °C. In addition, increase in steam injection pressure and time could further promote the degradation of main components. Difference in the manufacturing process significantly affected the properties of boards. In the case of steam injection, the temperature of boards increased rapidly by injecting high-pressure steam, and components degraded and then re-reacted in a very short period of time. In the case of hot pressing, it worked less efficiently since it took time for the steam to be generated from moisture in particles (Widyorini et al. 2005c). Similar observation revealed that particleboards made from sugarcane bagasse by steam injection pressing showed relatively better properties than by hot pressing (Widyorini et al.

2005b). However, it was suggested that excessive steam resulted in serious decomposition of components and thus poor board properties.

Self-bonding mechanism of binderless fiberboards

No matter whether woody or non-woody raw materials, pretreatment operations seem to be necessary for their further application. Mechanical, chemical, biological and thermochemical pretreatments have been employed separately or conjunctively depending on the expected products (Samaniego et al. 2013; Boonstra 2008; Smith 2011). Given the difference of chemical and morphological properties of raw materials, moisture content, as well as manufacturing process, several self-bonding mechanisms of binderless fiberboards have been proposed (Pintiaux et al. 2015). In the case of hot pressing, understanding the chemistry of substrates thermal reaction may benefit the understanding of the bonding mechanisms. Several reactions such as hydrolysis, dehydration and oxidation upon heating have been observed. Hemicelluloses were suggested to be easily removed due to their less thermal stability than cellulose and lignin (Hill 2006; Xu et al. 2006; Inoue et al. 1993; Rowell and McSweeny 2008). Organic acid, acetone and furfural were formed from the thermal decomposition of hemicelluloses (Tshabalala et al. 2012). However, Okuda et al. (2006a) compared the chemical compositions of kenaf core and obtained binderless fiberboards. They observed that little furfurals were formed during the preparation of binderless fiberboards (Okuda et al. 2006a). The discrepancy was probably the results of variations of detailed conditions, since the degradation of hemicelluloses has been reported to be highly dependent on moisture content, temperature, time of treatment and the composition of raw materials (Rowell and McSweeny 2008). Furthermore, Okuda et al. (2006a) suggested that components decomposed from lignin during hot pressing could be extracted by methanol, indicating little contribution to self-bonding. They believed that condensation reactions in lignin and chemical reaction from conjugated carbonyl compounds played an important role in self-bonding (Okuda et al. 2006a). More recently, Alvarez et al. (2015) suggested that these organic extractives from leaf plantain decreased the reactivity of the surface of the fibers. Removal of organic extractives favored the contact between fibers. As a result, an increase in the mechanical properties of binderless boards was observed (Alvarez et al. 2015). Conversely, removal of water extractives showed negative effects on the mechanical properties of boards. These water extractives with low molecular weight facilitated the formation of stable free radicals and therefore better bonding. In addition, Sun et al. (2014) comparatively characterized lignin from raw materials and binderless fiberboards prepared under hot pressing, respectively. Gel permeation chromatography (GPC) analysis revealed that molecular weight of enzymatic/mild acidolysis lignin (EMAL) decreased from 2210 to 1630 g/mol. They also observed the formation of β-O-4 linkages in EMAL after the production of fiberboards via NMR (Sun et al. 2014). In the case of steam exposition, self-bonding mechanism seems to be more complex due to the presence of steam treatment (Fig. 2). Although Quintana et al. (2009) observed no obvious cellulose degradation, depolymerization of hemicelluloses, lignin and cellulose has

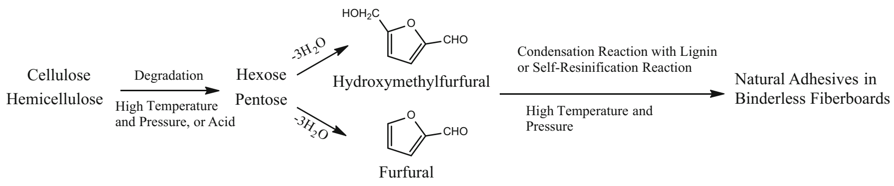

Fig. 2 Potential self-bonding mechanism in the production of binderless fiberboards with steam pretreatment (Fahmy and Mobarak 2013; Sun et al. 2014; Suzuki et al. 1998; Tshabalala et al. 2012)

been widely accepted during the steam treatments (Sun et al. 2005; Takashashi et al. 2010). After investigating the chemical changes of steam injection and hot pressing, Widyorini et al. (2005b) attributed the satisfactory performance of binderless particleboards using steam injection pressing to significant degradation of cellulose, hemicelluloses and lignin. Several researchers have noticed that the content of free sugars generated from hemicelluloses during steam pretreatment of lignocellulosic materials experienced an increase to maximum and then decreased in the yield. This indicated potential reactions of these sugars to other products (Rowell and McSweeny 2008; Lawther et al. 1996). Furthermore, furan monomers were found during the production of fiberboard (Cristescu and Karlsson 2013; Fahmy and Mobarak 2013; Tshabalala et al. 2012). These monomers were believed to generate lignin–furfural linkages or undergo self-polymerization during the pressing, which provided the main self-bonding strength of binderless fiberboards (Suzuki et al. 1998; Yan et al. 1996). On the other hand, physical perspectives of materials have been observed to contribute to self-bonding. Cellulose can be hydrolyzed during steam pretreatment, and these new crystals work as reinforcement for the lignin/hemicelluloses matrix, as well as contributing to the shape fixation and water resistance (Ito et al. 1998; Saito et al. 2013). Furthermore, it was also suggested that thermal softening of lignin played an important role in the properties of fiberboards (Okuda et al. 2006b; Van Dam et al. 2004). Bouajila et al. (2005) believed that in situ plasticization of lignin could increase the final mechanical properties.

Although several acceptable mechanisms have been suggested to play an important role in the self-bonding, these observations were mainly based on the chemical changes of components before and after the production of fiberboards. Information on the chemical changes during the production of fiberboards is limited. Therefore, the optimization of pressing variables, such as pressure and temperature as a function of time, is difficult. Previous works by the authors have investigated the surface composition of wood fibers (*Bixa orellana*) using XPS. Raw materials were subjected to hot pressing in a high-pressure reactor as a simulation of real manufacturing process. The effect of hot pressing on the concentration of carbonyl groups is shown in Fig. 3. Obviously, carbonyl groups content increased as the reaction proceeded within 2 min. This indicated that the degradation of cellulose and hemicelluloses to monosaccharides during hot pressing occurred. Additionally, the generation of furan monomers from dehydration of monosaccharides was also suggested to contribute to the increase in carbonyl groups content (Tshabalala et al. 2012). Then, carbonyl groups content gradually decreased until 6 min due to the

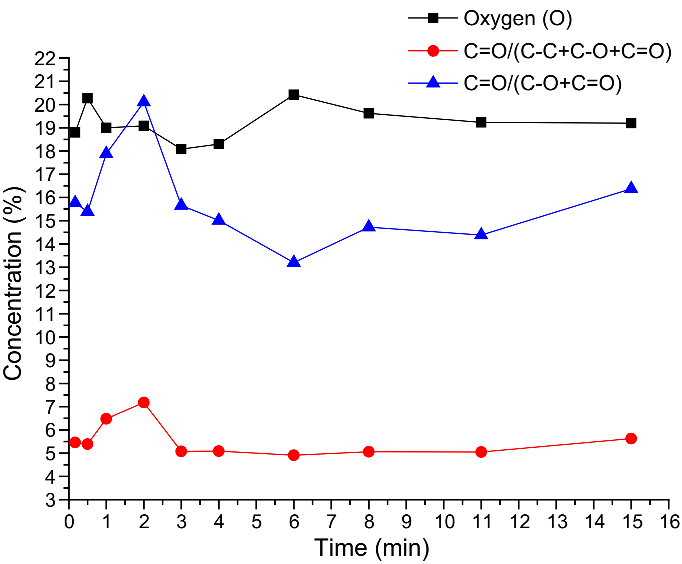

Fig. 3 Effect of hot pressing on the carbonyl groups content on the surface of fibers (*Bixa orellana* fibers, moisture 8 %, temperature 200 °C, pressure 7 MPa)

potential reaction of furan monomers. Self-bonding was achieved during this period. Finally, concentration of carbonyl groups slightly increased probably as the result of degradation of resin under continuous high pressure and temperature. These results obtained from XPS analysis of functional groups on the surface of fibers supported the observations that furan monomers were one of the main contributors to self-bonding of binderless fiberboards. Future work about the role of lignin and its degraded fractions in self-bonding is still needed.

Future researches

Although researches on the production of binderless fiberboards have been ongoing for many years, it is still challenging to scale up their production from bench scale to pilot and industry levels. The obstacle which limited its commercialization is the difficulties in elucidation of self-bonding mechanism of binderless fiberboards. Therefore, the cost and the performance of products are not competitive with commercial resin-based fiberboards. In view of traditional resin-based fiberboards which are environmentally unfriendly, efforts to reduce the cost and improve the physical and mechanical properties of binderless fiberboards still need to be continued. This review here may offer a new insight to figure out the self-bonding mechanisms, particularly the role of lignin and furan during hot pressing process via state-of-the-art technologies in terms of FT-IR, XPS and solid-state NMR. On the other hand, extensive efforts should also be put on the investigation of other efficient approaches to prepare binderless fiberboards, such as laccase-mediator

system, as well as effective pretreatment methods to utilize natural components in the fibers.

Acknowledgments The authors appreciate financial supports from National Natural Science Foundation of China (No. 51273211 and 51103171), the Ministry of Science and Technology of China (No. 2012AA03A605, 2012DFR50470 and 2014BAJ02B02), Bureau of Science and Technology of Ningbo (No. 2014B81004, 2014S10007, 2014B70023 and 2013C910012) and Ningbo Natural Science Foundation (No. 2014A610137, 2014A610138 and 2014A610194).

References

Alvarez C, Rojas OJ, Rojano B, Ganan P (2015) Development of self-bonded fiberboards from fiber of leaf plantain: effect of water and organic extractives removal. BioResource 10(1):672–683

Álvarez C, Rojano B, Almaza O, Rojas OJ, Gañán P (2011) Self-bonding boards from plantain fiber bundles after enzymatic treatment: adhesion improvement of lignocellulosic products by enzymatic pre-treatment. J Polym Environ 19(1):182–188

Angles MN, Reguant J, Montane D, Ferrando F, Farriol X, Salvado J (1999) Binderless composites from pretreated residual softwood. J Appl Polym Sci 73(12):2485–2491

Anglès M, Ferrando F, Farriol X, Salvadó J (2001) Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. Biomass Bioenergy 21(3):211–224

Baskaran M, Hashim R, Said N, Raffi SM, Balakrishnan K, Sudesh K, Sulaiman O, Arai T, Kosugi A, Mori Y (2012) Properties of binderless particleboard from oil palm trunk with addition of polyhydroxyalkanoates. Compos Part B-Eng 43(3):1109–1116

Boon JG, Hashim R, Sulaiman O, Hiziroglu S, Sugimoto T, Sato M (2013) Influence of processing parameters on some properties of oil palm trunk binderless particleboard. Holz Roh Werkst 71(5):583–589

Boonstra MJ (2008) A two-stage thermal modification of wood. Dissertation, Ghent University

Bouajila J, Limare A, Joly C, Dole P (2005) Lignin plasticization to improve binderless fiberboard mechanical properties. Polym Eng Sci 45(6):809–816

Chow S (1972) Thermal reactions and industrial uses of bark. Wood Fiber Sci 4(3):130–138

Chow S (1975) Bark boards without synthetic resins. For Prod J 25(11):32–37

Cristescu C, Karlsson O (2013) Changes in content of furfurals and phenols in self-bonded laminated boards. BioResources 8(3):4056–4071

Euring M, Rühl M, Ritter N, Kües U, Kharazipour A (2011a) Laccase mediator systems for eco-friendly production of medium-density fiberboard (MDF) on a pilot scale: physicochemical analysis of the reaction mechanism. Biotechnol J 6(10):1253–1261

Euring M, Trojanowski J, Horstmann M, Kharazipour A (2011b) Studies of enzymatic oxidation of TMP-fibers and lignin model compounds by a laccase-mediator-system using different ^{14}C and ^{13}C techniques. Wood Sci Technol 46(4):699–708

Euring M, Trojanowski J, Kharazipour A (2013) Laccase-mediator catalyzed modification of wood fibers: studies on the reaction mechanism and making of medium-density fiberboard. For Prod J 63(1–2):54–60

Fahmy TA, Mobarak F (2013) Advanced binderless board-like green nanocomposites from undebarked cotton stalks and mechanism of self-bonding. Cellulose 20(3):1453–1457

Felby C, Nielsen BR, Olesen PO, Skibsted LH (1997a) Identification and quantification of radical reaction intermediates by electron spin resonance spectrometry of laccase-catalyzed oxidation of wood fibers from beech (*Fagus sylvatica*). Appl Microbiol Biot 48(4):459–464

Felby C, Pedersen LS, Nielsen BR (1997b) Enhanced auto adhesion of wood fibers using phenol oxidases. Holzforschung 51(3):281–286

Felby C, Hassingboe J, Lund M (2002) Pilot-scale production of fiberboards made by laccase oxidized wood fibers: board properties and evidence for cross-linking of lignin. Enzyme Microb Tech 31(6):736–741

Felby C, Thygesen LG, Sanadi A, Barsberg S (2004) Native lignin for bonding of fiber boards—evaluation of bonding mechanisms in boards made from laccase-treated fibers of beech (*Fagus sylvatica*). Ind Crop Prod 20(2):181–189

Gao Z, Wang XM, Wan H, Brunette G (2011) Binderless panels made with black spruce bark. BioResources 6(4):3960–3972

Geimer RL, Price EW (1987) Steam injection pressing: large panel fabrication with southern hardwoods. In: Proceedings of the 20th international particleboard/composite materials symposium; 1986 April 8–10. Washington State University, Pullman, 1986, pp 367–384

Geng X, Zhang S, Deng J (2006) Alkaline treatment of black spruce bark for the manufacture of binderless fiberboard. J Wood Chem Technol 26(4):313–324

Gupta G, Ning Y, Feng MW (2011) Effects of pressing temperature and particle size on bark board properties made from beetle-infested lodgepole pine (*pinus contorta*) barks. Forest Prod J 61(6):478–488

Halvarsson S, Edlund H, Norgren M (2009) Manufacture of non-resin wheat straw fibreboards. Ind Crop Prod 29(2):437–445

Hashim R, Saari N, Sulaiman O, Sugimoto T, Hiziroglu S, Sato M, Tanaka R (2010) Effect of particle geometry on the properties of binderless particleboard manufactured from oil palm trunk. Mater Design 31(9):4251–4257

Hidayat H, Keijsers E, Prijanto U, van Dam J, Heeres H (2014) Preparation and properties of binderless boards from *Jatropha curcas* L. seed cake. Ind Crop Prod 52:245–254

Hill CAS (2006) Wood modification: chemical, thermal and other processes. Wiley, Chichester

Hüttermann A, Mai C, Kharazipour A (2001) Modification of lignin for the production of new compounded materials. Appl Microbiol Biot 55(4):387–394

Imam SH, Gordon SH, Mao L, Chen L (2001) Environmentally friendly wood adhesive from a renewable plant polymer: characteristics and optimization. Polym Degrad Stabil 73(3):529–533

Inoue M, Norimoto M, Tanahashi M, Rowell RM (1993) Steam or heat fixation of compressed wood. Wood Fiber Sci 25(3):224–235

Ito Y, Tanahashi M, Shigematsu M, Shinoda Y (1998) Compressive-molding of wood by high-pressure steam-treatment: part 1. Development of compressively molded squares from thinnings. Holzforschung 52(2):211–216

Kharazipour A, Euring M (2010) Use of mediators in the production of fibreboards. WO 2010020409 A3

Kharazipour A, Euring M (2013) Method for producing wood materials and/or composite materials. WO 2013127947 A1

Kharazipour A, Hüttermann A, Lüdemann H (1997) Enzymatic activation of wood fibres as a means for the production of wood composites. J Adhes Sci Technol 11(3):419–427

Kharazipour A, Bergmann K, Nonninger K, Hüttermann A (1998) Properties of fibre boards obtained by activation of the middle lamella lignin of wood fibres with peroxidase and H_2O_2 before conventional pressing. J Adhes Sci Technol 12(10):1045–1053

Kudanga T, Prasetyo EN, Sipila J, Nousiainen P, Widsten P, Kandelbauer A, Nyanhongo GS, Guebitz GM (2008) Laccase-mediated wood surface functionalization. Eng Life Sci 8(3):297–302

Kudanga T, Nyanhongo GS, Guebitz GM, Burton S (2011) Potential applications of laccase-mediated coupling and grafting reactions: a review. Enzyme Microb Tech 48(3):195–208

Kües U, Bohn C, Euring M, Müller C, Polle A, Kharazipour A (2007) Enzymatically modified wood in panel board production. In book: wood production, wood technology, and biotechnological impacts. Universitätsverlag Göttingen, pp 433–468

Kumar R, Choudhary V, Mishra S, Varma I, Mattiason B (2002) Adhesives and plastics based on soy protein products. Ind Crop Prod 16(3):155–172

Kwon JH, Geimer RL (1998) Impact of steam pressing variables on the dimensional stabilization of flakeboard. For Prod J 48(4):55–61

Laemsak N, Okuma M (2000) Development of boards made from oil palm frond II: properties of binderless boards from steam-exploded fibers of oil palm frond. J Wood Sci 46(4):322–326

Lamaming J, Sulaiman O, Sugimoto T, Hashim R, Said N, Sato M (2013) Influence of chemical components of oil palm on properties of binderless particleboard. BioResources 8(3):3358–3371

Lawther M, Sun RC, Banks WB (1996) Effect of steam treatment on the chemical composition of wheat straw. Holzforschung 50(4):365–371

Lee CM, Hunt JF (2013) Binderless panel made from wood particles and cellulosic fibers, US Patents 594,921

Luo H, Yue L, Wang NW, Zhang HY, Lu XN (2014) Manufacture of binderless fiberboard made from bamboo processing residues by steam explosion pretreatment. Wood Res 59(5):861–870

Mai C, Kües U, Militz H (2004) Biotechnology in the wood industry. Appl Microbiol Biot 63(5):477–494

Mancera C, Ferrando F, Salvado J (2008) *Cynara cardunculus* as raw material for the production of binderless fiberboards: optimization of pretreatment and pressing conditions. J Wood Chem Technol 28(3):207–226

Mancera C, Mansouri NEE, Ferrando F, Salvado J (2011) The suitability of steam exploded *Vitis vinifera* and alkaline lignin for the manufacture of fiberboard. BioResources 6(4):4439–4453

Mansouri NEE, Pizzi A, Salvado J (2007) Lignin-based polycondensation resins for wood adhesives. J Appl Polym Sci 103(3):1690–1699

Matuana L, Balatinecz J, Sodhi R, Park C (2001) Surface characterization of esterified cellulosic fibers by XPS and FTIR spectroscopy. Wood Sci Technol 35(3):191–201

Mejía EH, Quintana GC, Ogunsile BO (2014) Development of binderless fiberboards from steam-exploded and oxidized oil palm wastes. BioResources 9(2):2922–2936

Mobarak F, Fahmy Y, Augustin H (1982) Binderless lignocellulose composite from bagasse and mechanism of self-bonding. Holzforschung 36(3):131–136

Müller C, Euring M, Kharazipour A (2009) Enzymatic modification of wood fibres for activating their ability of self bonding. Int J Mater Prod Tec 36(1):189–199

Nasir M, Gupta A, Beg M, Chua GK, Jawaid M, Kumar A, Khan TA (2013) Fabricating eco-friendly binderless fiberboard from laccase-treated rubber wood fiber. BioResources 8(3):3599–3608

Nikvash N, Kharazipour A, Euring M (2012) Effects of wheat protein as a biological binder in the manufacture of particleboards using a mixture of canola, hemp, bagasse, and commercial wood. For Prod J 62(1):49–57

Nikvash N, Kharazipour A, Euring M (2013) Low density particleboards with different kind annual plants by UF/wheat protein adhesives. Holzforschung 54(2):29–35

Nyanhongo GO, Kudanga T, Prasetyo EN, Guebitz GM (2010) Mechanistic insights into laccase-mediated functionalisation of lignocellulose material. Biotechnol Genet Eng 27:305–329

Okamoto H, Sano S, Kawai S, Okamoto T, Sasaki H (1994) Production of dimensionally stable medium density fiberboard by use of high-pressure steam pressing. Mokuzai Gakkaishi 40:380–389

Okuda N, Hori K, Sato M (2006a) Chemical changes of kenaf core binderless boards during hot pressing (I): influence of the pressing temperature condition. J Wood Sci 52(3):244–248

Okuda N, Hori K, Sato M (2006b) Chemical changes of kenaf core binderless boards during hot pressing (II): effects on the binderless board properties. J Wood Sci 52(3):249–254

Pereira L, Bastos C, Tzanov T, Cavaco PA, Guebizt GM (2005) Environmentally friendly bleaching of cotton using laccases. Environ Chem Lett 3(2):66–69

Pintiaux T, Viet D, Vandenbossche V, Rigao L, Rouilly A (2015) Binderless materials obtained by thermo-compressive processing of lignocellulosic fibers : a comprehensive review. BioResource 10(1):1915–1963

Quintana G, Velasquez J, Betancourt S, Ganan P (2009) Binderless fiberboard from steam exploded banana bunch. Ind Crop Prod 29(1):60–66

Rammon R, Kelley S, Young R, Gillespie R (1982) Bond formation by wood surface reactions part II. Chemical mechanisms of nitric acid activation. J Adhesion 14(3–4):257–282

Riquelme-Valdes J, Ramirez E, Contreras D, Freer J, Rodriguez J (2008) Fiberboard manufactured without resin using the Fenton reaction. J Chil Chem Soc 53(4):1722–1725

Rowell RM, McSweeny JD (2008) Heat treatments of wood fibers for self-bonding and stabilized fiberboards. Mol Cryst Liq Cryst 483(1):307–325

Saadaoui N, Rouilly A, Fares K, Rigal L (2013) Characterization of date palm lignocellulosic by-product and self-bonding composite materials obtained thereof. Mater Design 50:302–308

Saari N, Hashim R, Sulaiman O, Hiziroglu S, Sato M, Sugimoto T (2014) Properties of steam treated binderless particleboard made from oil palm trunks. Compos Part B-Eng 56:344–349

Saheb DN, Jog J (1999) Natural fiber polymer composites: a review. Adv Polym Tech 18(4):351–363

Saito Y, Ishii M, Sato M (2013) The suitable harvesting season and the part of moso bamboo (*Phyllostachys pubescens*) for producing binderless boards. Wood Sci Technol 47(5):1071–1081

Salthammer T, Mentese S, Marutzky R (2010) Formaldehyde in the indoor environment. Chem Rev 110(4):2536–2572

Samaniego MRP, Yadama V, Lowell E, Herrera RE (2013) A review of wood thermal pretreatments to improve composite properties. Wood Sci Technol 47:1285–1319

Schmidt A, Mallon S, Thomsen AB, Hvilsted S, Lawther J (2002) Comparison of the chemical properties of wheat straw and beech fibers following alkaline wet oxidation and laccase treatments. J Wood Chem Technol 22(1):39–53

Schopper C, Kharazipour (2006) Development of a wheat protein based adhesive for the production of medium density fiberboards. Review of forest, wood products and wood biotechnology of Iran and Germany. Institute of Forest Botany, Georg-August-University Gottingen, Germany, pp 10–19

Shao S, Jin Z, Wen G, Iiyama K (2009) Thermo characteristics of steam-exploded bamboo (*Phyllostachys pubescens*) lignin. Wood Sci Technol 43(7–8):643–652

Shen KC (1986) Process for manufacturing composite products from lignocellulosic materials, US Patents 4,627,951

Smith AJ (2011) Hot water extraction and subsequent Kraft pulping for pine wood chips. Dissertation, Auburn University, Auburn

Sreekala M, Kumaran M, Joseph S, Jacob M, Thomas S (2000) Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. Appl Compos Mater 7(5–6):295–329

Subramanian R, Balaba W, Somasekharan K (1982) Surface modification of wood using nitric acid. J Adhesion 14(3–4):295–304

Suchsland O, Woodson G, McMillin CW (1985) Binderless fiberboard from two different types of fiber furnishes. For Prod J 35(2):63–68

Sun XF, Xu F, Sun RC, Fowler P, Baird MS (2005) Characteristics of degraded cellulose obtained from steam-exploded wheat straw. Carbohydr Res 340(1):97–106

Sun YC, Lin Z, Peng WX, Yuan TQ, Xu F, Wu YQ, Yang J, Wang YS, Sun RC (2014) Chemical changes of raw materials and manufactured binderless boards during hot pressing: lignin isolation and characterization. BioResources 9(1):1055–1071

Suzuki S, Shintani H, Park SY, Saito K, Laemsak N, Okuma M, Iiyama K (1998) Preparation of binderless boards from steam exploded pulps of oil palm (*Elaeis guneensis* Jaxq) fronds and structural characteristics of lignin and wall polysaccharides in steam exploded pulps to be discussed for self-bindings. Holzforschung 52(4):417–426

Takashashi I, Sugimoto T, Takasu Y, Yamasaki M, Sasaki Y, Kikata Y (2010) Preparation of thermoplastic molding from steamed Japanese beech flour. Holzforschung 64(2):229–334

Troughton GE, Lum C (2000) Pilot plant evaluation of steam-injection pressing for LVL and plywood products. For Prod J 50(1):25–28

Tshabalala MA, McSweeny JD, Rowell RM (2012) Heat treatment of wet wood fiber: a study of the effect of reaction conditions on the formation of furfurals. Wood Mat Sci Eng 7(4):202–208

Van Dam JE, van den Oever MJ, Teunissen W, Keijsers ER, Peralta AG (2004) Process for production of high density/high performance binderless boards from whole coconut husk. Part 1: lignin as intrinsic thermosetting binder resin. Ind Crop Prod 19(3):207–216

Velasquez J, Ferrando F, Salvado J (2002) Binderless fiberboard from steam exploded *Miscanthus sinensis*: the effect of a grinding process. Holz als Roh-und Werkstoff 60(4):297–302

Velasquez J, Ferrando F, Farriol X, Salvado J (2003) Binderless fiberboard from steam exploded *Miscanthus sinensis*. Wood Sci Technol 37(3–4):269–278

Wellons J, Krahmer R (1973) Self bonding in bark composites. Wood Sci 6(2):112–122

Widsten P (2002) Oxidative activation of wood fibers for the manufacture of medium-density fiberboard (MDF). Helsinki University of Technology, Helsinki

Widsten P, Kandelbauer A (2008) Adhesion improvement of lignocellulosic products by enzymatic pre-treatment. Biotechnol Adv 26(4):379–386

Widsten P, Qvintus LP, Tuominen S, Laine JE (2003) Manufacture of fiberboard from wood fibers activated with Fentons reagent ($H_2O_2/FeSO_4$). Holzforschung 57(4):447–452

Widyorini R, Higashihara T, Xu J, Watanabe T, Kawai S (2005a) Self-bonding characteristics of binderless kenaf core composites. Wood Sci Technol 39(8):651–662

Widyorini R, Xu J, Umemura K, Kawai S (2005b) Manufacture and properties of binderless particleboard from bagasse I: effects of raw material type, storage methods, and manufacturing process. J Wood Sci 51(6):648–654

Widyorini R, Xu J, Watanabe T, Kawai S (2005c) Chemical changes in steam-pressed kenaf core binderless particleboard. J Wood Sci 51(1):26–32

Xu JY, Han G, Wong E, Kawai S (2003) Development of binderless particleboard from kenaf core using steam-injection pressing. J Wood Sci 49(4):327–332

Xu JY, Widyorini R, Kawai S (2005) Properties of kenaf core binderless particleboard reinforced with kenaf bast fiber-woven sheets. J Wood Sci 51(4):415–420
Xu JY, Widyorini R, Yamauchi H, Kawai S (2006) Development of binderless fiberboard from kenaf core. J Wood Sci 52(3):236–243
Yan H, Cao Z, Guo W (1996) Study on bonding mechanism of dry-process binderless fiberboards part I. Chemical changes and effects in binderless fiberboard manufacture. For Ind 10(4):3–11
Yau ST, Thomas BR, Galkin O, Gliko O, Vekilov PG (2006) Lignin-based polycondensation resins for wood adhesives. J Appl Polym Sci 103(3):1690–1699
Ye XP, Julson J, Kuo M, Womac A, Myers D (2007) Properties of medium density fiberboards made from renewable biomass. BioResource Technol 98(5):1077–1084
Young R, Rammon R, Kelley S, Gillespie R (1982) Bond formation by wood surface reaction: part I. Surface analysis by ESCA. Wood Sci 14(3):110–119
Young RA, Fujita M, River BH (1985) New approaches to wood bonding: a base-activated lignin adhesive system. Wood Sci Technol 19(4):363–381
Zadorecki P, Michell AJ (1989) Future prospects for wood cellulose as reinforcement in organic polymer composites. Polym Composite 10(2):69–77
Zhang A, Chen Z, Fan Q, Shao C (2013) A method to produce high density binderless fiberboards. China Patents 201,210,541,382.X
Zhang A, Chen Z, Shao C, Song H, Wu K (2014a) A method to manufacture binderless fiberboards made from wood fibers. China Patents 201,110,411,549.6
Zhang A, Han Z, Xue L (2014b) A non-formaldehyde wood fiberboard production methods, China Patents 201,410,076,627.5
Zhou X, Zheng F, Lv C, Tang L, Wei K, Liu X, Du G, Yong Q, Xue G (2013) Properties of formaldehyde-free environmentally friendly lignocellulosic composites made from poplar fibres and oxygen-plasma-treated enzymatic hydrolysis lignin. Compos Part B-Eng 53:369–375